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Sulfur Dioxide Flux into Leaves of 'Geranium carolinianum' L.: Evidence for a Nonstomatal or Residual Resistance

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16. ABSTRACT

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Sulfur Dioxide Flux into Leaves of *Geranium carolinianum* L.[1]

EVIDENCE FOR A NONSTOMATAL OR RESIDUAL RESISTANCE

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ABSTRACT

The concurrent exchange of SO_2 and H_2O vapor between the atmosphere and foliage of *Geranium carolinianum* was investigated using a whole-plant gas exchange chamber. Total leaf flux of SO_2 was partitioned into leaf surface and internal fractions. The emission rate of SO_2-induced H_2S was measured to develop a net leaf budget for atmospherically derived sulfur. Stomatal resistance to SO_2 flux was estimated by two techniques: (a) $R_s^{SO_2}$ from SO_2 data using analog modeling techniques and (b) $R_s^{SO_2}$ from analogy to H_2O (*i.e.* 1.89 $R_s^{H_2O}$).

The emission of H_2S was positively correlated with the rate of SO_2 flux into the leaf interior. An accounting of the simultaneous, bidirectional flux of gaseous sulfur compounds during pollutant exposure showed that sulfur accumulation in the leaf interior of *G. carolinianum* was 7 to 15% lower than that estimated solely from mass-balance calculations of SO_2 flux data (*i.e.* ignoring H_2S emissions).

The esimate of stomatal resistance to pollutant flux from the SO_2 data ($R_s^{SO_2}$) was consistently less than the simultaneous estimate derived from analogy to H_2O vapor ($R_s^{SO_2}$). The resultant of $R_s^{SO_2} - R_s^{SO_2}$, which was always negative, is indicative of a residual resistance to SO_2 flux into the leaf interior. On a comparative basis, SO_2 molecules experienced less pathway resistance to diffusion than effluxing H_2O molecules. It is proposed that the SO_2:H_2O path length ratio is less than unity, as a consequence of the pollutant's high water solubility and unique chemical reactivity in solution. Thus, the diffusive paths for H_2O and SO_2 in *G. carolinianum* are not completely synonymous.

Gas phase resistance, principally at the stomate, is thought to be the predominant factor limiting the diffusion of most pollutant gases including SO_2 (24, 46). However, because the path of influxing pollutant molecules extends into the aqueous phase within cells of the leaf interior, the flux of pollutant molecules may be influenced by factors (*i.e.* residual resistance) not shared by effluxing H_2O molecules (42). The potential importance of these residual factors in controlling SO_2 flux into the leaf interior is recognized (14, 23, 43). Unequal SO_2 flux into leaves of corn (*Zea mays*) and pea (*Pisum sativum*) was not attributed to stomatal resistance but rather to physicochemical properties of the mesophyll tissue that imparted a greater SO_2 sink capacity in pea as compared with corn (19). More recently, Hällgren *et al.* (15) observed changes in SO_2 flux to needles of scots pine (*Pinus sylvestris*) that were not correlated with stomatal responses.

Estimates of SO_2 flux into the leaf interior are frequently calculated from the ratio of the atmospheric SO_2 concentration to gas phase resistance to SO_2, the latter being derived from the sum of boundary layer and stomatal resistance to H_2O. This assumes (a) an SO_2 concentration of zero in the leaf interior, (b) a combined gas and aqueous pathway resistance to SO_2 that is analogous to H_2O including an identical path length, and (c) an accurate analytical measurement of SO_2 without interference from other sulfur-containing gases. Accurate SO_2 measurement is important because SO_2-exposed plants emit H_2S in the light (5), which is indistinguishable from SO_2 by flame photometry (38), a common technique for measuring SO_2. Because this technique measures all sulfur species in the air stream, the concentration gradient for SO_2 is overestimated. Moreover, mass-balance calculations of SO_2 flux to foliage would be in error (underestimated) because the true chamber/cuvette outlet SO_2 concentration is less than the instrument reading. To investigate the factors controlling SO_2 flux into the leaf interior, the concurrent fluxes of H_2O, SO_2, and H_2S were measured in foliage of *Geranium carolinianum* exposed to a range of SO_2 concentrations. The extent to which pathway resistance to SO_2 can be fully derived from H_2O was assessed using analog modeling techniques.

MATERIALS AND METHODS

Geranium carolinianum, an annual herbaceous species, was grown from seed in a Jiffy Mix:Perlite (1/2, v/v) mixture. Initially, plants were grown in a glasshouse under maximum day temperature of 28°C and mean night temperature of 20°C. The photoperiod was extended to 16 h with HID Sodium Vapor Lamps. North Carolina State University Phytotron Nutrient Solution (6) was applied daily. Two weeks before the experiment, plants were transferred to a controlled environmental unit with climatic and atmospheric conditions (excluding pollutants) similar to that of the gas exchange chamber.

Gas exchange measurements were made in an open system using a mass-balance approach (40). At the chamber's inlet and outlet ports, the concentration of H_2O was measured with a dewpoint hygrometer (CTE model 84P Sensor and 84A Hygrometer; Electromech Services, Sunnyvale, CA) calibrated with an ice bath. The concentrations of SO_2 and H_2S were measured with a flame photometric sulfur gas analyzer (Sulfur Monitor model 8450; Monitor Labs, San Diego, CA) equipped with an H_2S scrubber (model 8740, Monitor Labs). The scrubber's selectivity for H_2S was determined using mixtures of H_2S and SO_2 in

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charcoal-filtered air. The sulfur gas analyzer was calibrated daily with SO_2 from a permeation tube (Permacal 8500, Monitor Labs). To eliminate in-line condensation of H_2O and subsequent SO_2 deposition, the stainless steel sample lines were heated above the dewpoint. Outlet CO_2 concentration (345 ± 20 $\mu l\ l^{-1}$) was monitored with an IRGA (model 65, Beckman Instruments Co.) calibrated with standard gases over a 250 to 400 $\mu l\ l^{-1}$ concentration range. Copper-constantan thermocouples provided shielded air (26 ± 1°C) and leaf (daylight: 27 ± 1.5°C) temperatures and were read on a digital thermometer (model 2176A; Omega Engineering Inc., Stanford, CT; with a 0.1°C resolution). The RH in both light and dark conditions was 75 ± 8%. The photosynthetic photon flux density (PPFD) was 490 $\mu E\ m^{-2}\ s^{-1}$.

Ambient air was filtered, scrubbed, conditioned (air and dewpoint temperature), mixed with concentrated SO_2 (Matheson Gas Co., East Rutherford, NJ), and delivered to the chamber at a rate of 100 $cm^3\ s^{-1}$ providing an air exchange every 2.8 min. The cylindrical Plexiglas chamber was housed in a controlled environmental unit. An airtight baseplate was used to separate the above-ground portion of the plant from the pot. Within the chamber, rapid air mixing was maintained by wall baffles and fan blades rotated by an externally mounted electric motor (40). Air turbulence caused slight leaf flutter throughout the plant canopy. Experiments were conducted when the plants had 8 to 14 rosette leaves. A single plant was kept in the gas exchange chamber for 24 h. The first 14 h was a pollution-free acclimatization period. Exposures to SO_2 began in the last 5 h of the dark period and continued through the light period. The SO_2 concentration at the outlet port for any single exposure was held constant over the dark-to-light exposure regime. The exposure concentrations ranged from 0.3 to 0.8 $\mu l\ l^{-1}$ and were specific for SO_2 (*i.e.* H_2S contribution to total sulfur concentration at outlet port was removed). Gaseous fluxes and leaf resistances to H_2O and SO_2 (see below) were calculated from data recorded at 0.5-h intervals. Following exposure, leaf area (one surface) was determined photooptically (Hayashi-Denko, Tokyo, Japan). A total of 118 plants were studied, and for any single pollutant concentration 9 to 21 plants were used. To provide further data on SO_2-induced H_2S, the emission rate of H_2S over an expanded range of SO_2 concentrations (0.1–1.0 $\mu l\ l^{-1}$) was investigated in a separate set of plants ($n = 11$).

The techniques to analyze simultaneous fluxes of H_2O, SO_2, and H_2S are outlined in principle by Sestak *et al.* (34); the following are particularly relevant features. Total flux of a gas to or from the plant (J^{Gas}_{TOTAL} in nmol gas $cm^{-2}\ h^{-1}$) was calculated as

$$J^{Gas}_{TOTAL} = | C^{Gas}_{Inlet} - C^{Gas}_{Outlet} | \cdot F \cdot A^{-1} \quad (1)$$

where C^{Gas} was gas concentration (nmol cm^{-3}) at the inlet and outlet ports, F was flow rate ($cm^3\ s^{-1}$) through the chamber, and A was leaf area (cm^2). Flux estimates for each plant were calculated in the dark and light for SO_2 and H_2O, and in the light only for H_2S (H_2S was not emitted in the dark). In the light, $J^{SO_2}_{TOTAL}$ was the summation of SO_2 flux to the leaf surface ($J^{SO_2}_{SURFACE}$) and interior ($J^{SO_2}_{INTERNAL}$). To determine the latter, flux in the light was reduced by the magnitude of flux in the preceding dark period. Because SO_2 is highly soluble in water, the outlet dewpoint in the dark was maintained equivalent to that in the light by injecting small amounts of steam to simulate transpiration. Deposition of SO_2 to the chamber interior was experimentally determined for a range of SO_2 concentrations by simulating transpiration (steam injection) in both the dark and light in an empty chamber maintained at the same conditions (temperature, light, RH) as that with plants.

Leaf resistance to diffusion of each gas (R^{Gas}_L in s cm^{-1}) from or into the leaf interior was estimated as the product of the concentration gradient from the atmosphere (C^{Gas}_a) to leaf interior (C^{Gas}_i) and the reciprocal of flux:

$$R^{Gas}_L = | C^{Gas}_a - C^{Gas}_i | \cdot (J^{GAS})^{-1} \quad (2)$$

For H_2O, $C^{H_2O}_i$ was calculated from leaf temperature, assuming saturation. Boundary layer resistance ($R^{H_2O}_a$) was measured for a separate group of plants ($n = 10$) by the energy balance approach (34); $R^{H_2O}_a$ averaged 0.20 s cm^{-1}. Stomatal resistance to H_2O ($R^{H_2O}_s$) was calculated by subtraction of $R^{H_2O}_a$ from $R^{H_2O}_L$.

Stomatal resistance to SO_2 was estimated by two techniques. First, assuming an analogous diffusive pathway for SO_2 and H_2O (43),

$$R^{SO_2}_s = 1.89\ R^{H_2O}_s \quad (3)$$

where 1.89 was the ratio of diffusive coefficients of SO_2 to H_2O (see Appendix). The second technique was independent of H_2O and used an analog modeling approach (the path of influxing SO_2 molecules, sources of diffusive resistance, and concentration gradients are shown in Fig. 1). From equation (2), $R^{SO_2}_s$ (the prime identifies this estimate) was estimated as

$$R^{SO_2}_s = (C^{SO_2}_c - C^{SO_2}_i) \cdot (J^{SO_2}_{INTERNAL})^{-1} \quad (4)$$

where ($C^{SO_2}_c - C^{SO_2}_i$) was the concentration differential from the exterior of the stomate ($C^{SO_2}_c$) to the leaf interior ($C^{SO_2}_i = 0$) (see Appendix). Black and Unsworth (2) provide data in support of an internal SO_2 concentration equal to zero.

Gaastra (11) used this technique to investigate factors controlling CO_2 assimilation. Any difference in the two estimates of stomatal resistance to SO_2 is evidence for a residual resistance $R^{SO_2}_r$) to the diffusion of SO_2 into the leaf interior:

$$R^{SO_2}_r = R^{SO_2}_s - R^{SO_2}_s \quad (5)$$

The physical site(s) of this residual resistance to SO_2 may be in either the gaseous or aqueous phase of the diffusive path. The

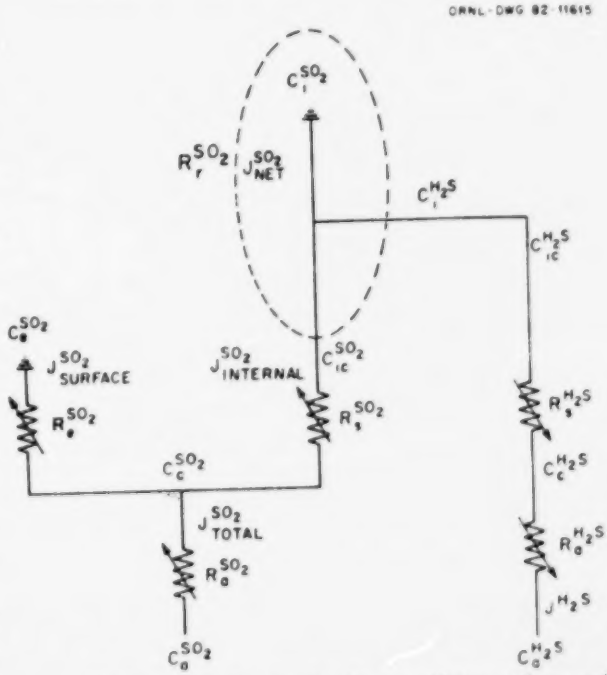

FIG. 1. Model of SO_2 flux showing the gas' diffusive pathway and source-to-sink concentrations and resistances. The counter-current flux of H_2S, which is SO_2-induced, is shown in analogous fashion. The dashed-line oval is the source of residual resistance ($R^{SO_2}_r$) to SO_2 flux. The symbols are defined in the Appendix.

series of equations derived from the analogy of SO_2 and H_2O flux to Ohm's Law is outlined (Appendix).

RESULTS

The Flux of SO_2 and H_2S. Total leaf flux of SO_2 ($J^{SO_2}_{TOTAL}$) ranged from 27 to 67 nmol cm^{-2} h^{-1} (Fig. 2a). This 2.5-fold range of $J^{SO_2}_{TOTAL}$ reflected the 2.7-fold increase in atmospheric SO_2 concentration (0.3–0.8 μl l^{-1}). Exposure time did not have a pronounced or consistent effect on $J^{SO_2}_{TOTAL}$. The corresponding range of leaf surface flux of SO_2 ($J^{SO_2}_{SURFACE}$) was 7 to 27 nmol cm^{-2} h^{-1} (Fig. 2b). As with $J^{SO_2}_{TOTAL}$, SO_2 concentration rather than exposure time was the principle source of variation. As a percentage of $J^{SO_2}_{TOTAL}$, $J^{SO_2}_{SURFACE}$ averaged 27 to 36%. Internal leaf flux of SO_2 ($J^{SO_2}_{INTERNAL}$) ranged from 18 to 44 nmol cm^{-2} h^{-1} and changed with both exposure time and SO_2 concentration (Fig. 2c). At 0.3 to 0.5 μl l^{-1} SO_2, $J^{SO_2}_{INTERNAL}$ at 4 h was 20 to 30% less than that at 1 h; exposure duration at the higher concentrations did not influence $J^{SO_2}_{INTERNAL}$.

The flux of H_2S from the leaf (J^{H_2S}) responded to the light regime, exposure duration, and SO_2 concentration. H_2S was not detected from plants exposed to SO_2 in the dark. With the onset of lights, H_2S was detected within 15 min; the concentration increased for the next 45 to 60 min and thereafter remained constant for 3 h (Fig. 2d). After 1 h in the light, J^{H_2S} ranged from 1.2 to 7.5 nmol cm^{-2} h^{-1}. Over the SO_2 concentration range of 0.1 to 1.0 μl l^{-1}, J^{H_2S} was marginally correlated ($r = +0.3$) with atmospheric SO_2 concentration. The regression of J^{H_2S} on $J^{SO_2}_{INTERNAL}$ (using log-transformed data) provided a linear regression model with a r^2 value of 0.84 (Fig. 3). The regression model suggests a threshold level of 19.1 nmol cm^{-2} h^{-1} for $J^{SO_2}_{INTERNAL}$ before detectable H_2S emissions were observed. As $J^{SO_2}_{INTERNAL}$ increased from 20 to 60 nmol cm^{-2} h^{-1}, the ratio of J^{H_2S} to $J^{SO_2}_{INTERNAL}$ rose from 0.05 to 0.33.

Leaf Budget of Sulfur. From simultaneous fluxes of SO_2 and H_2S, a leaf budget of sulfur following SO_2 exposure was calculated (Fig. 4). As a percentage of J^{Sulfur}_{TOTAL}, $J^{Sulfur}_{INTERNAL}$ fell within a range of 64 to 73%. The remainder of J^{Sulfur}_{TOTAL} was deposited to the leaf surface ($J^{Sulfur}_{SURFACE}$). Of the sulfur entering the leaf interior as SO_2 ($J^{Sulfur}_{INTERNAL}$), 7 to 15% was reemitted to the atmosphere as $J^{Sulfur}_{H_2S}$, and the percentage increased with SO_2 concentration. This reemission of sulfur resulted in a net sulfur loading in the leaf interior

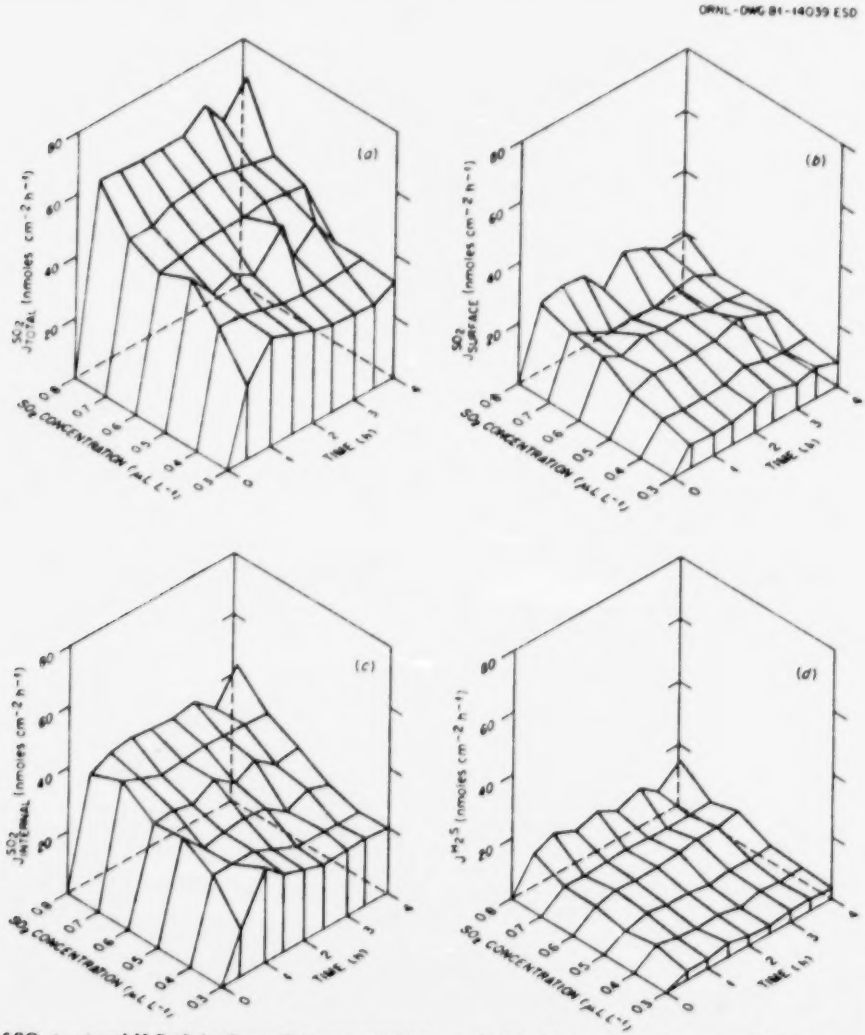

FIG. 2. The fluxes of SO_2 (a–c) and H_2S (d) in *G. carolinianum* at 0.5-h intervals (0.5–4 h) in atmospheres containing 0.3 to 0.8 μl l^{-1} SO_2. Total leaf flux or $J^{SO_2}_{TOTAL}$ (a) is partitioned into leaf surface or $J^{SO_2}_{SURFACE}$ (b) and interior or $J^{SO_2}_{INTERNAL}$ (c) fractions.

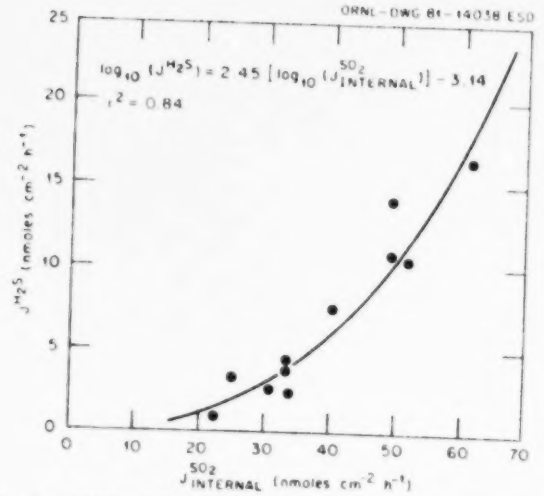

FIG. 3. Leaf flux of H_2S (J^{H_2S}) as a function of internal leaf flux of SO_2 ($J^{SO_2}_{INTERNAL}$).

(J^{Sulfur}_{NET}) of 22.2 to 34.2 nmol sulfur cm^{-2} h^{-1} at 0.3 and 0.8 μl l^{-1} SO_2, respectively.

Stomatal Resistance to SO_2 Flux. Over the range of SO_2 concentrations and exposure times in the light, $R_s^{SO_2}$ (via analogy to H_2O) ranged from 5.4 to 7.5 s cm^{-1} and averaged 6.2 s cm^{-1} ± 1.5 SD (Fig. 5a). This corresponds to a stomatal resistance to H_2O of 2.9 to 4.0 s cm^{-1} (mean = 3.3 s cm^{-1}). With the 4-h exposure, $R_s^{SO_2}$ was either unchanged with time (0.5 and 0.7 μl l^{-1} SO_2) or declined 11 to 19% (remaining concentrations). This estimate of stomatal resistance to SO_2 flux did not respond markedly to increasing SO_2 concentration in the atmosphere.

The second estimate of stomatal resistance based on SO_2 flux ($R_s^{SO_2}$) ranged from 1.0 to 3.9 s cm^{-1} (Fig. 5b). The mean $R_s^{SO_2}$ was 3.0 s cm^{-1} ± 0.8 SD, 52% lower than the mean estimate of stomatal resistance derived from analogy to H_2O. Over the 4-h exposure period in the light at all concentrations, $R_s^{SO_2}$ increased at least 31% (0.6 μl l^{-1}) and at most 120% (0.3 μl l^{-1}). As the SO_2 concentration increased, the influence of exposure time on $R_s^{SO_2}$ declined, and at 0.8 μl l^{-1} SO_2, $R_s^{SO_2}$ at 1 and 4 h was equivalent. At 1.5 h, $R_s^{SO_2}$ nearly doubled in magnitude (1.6–3.0 s cm^{-1}) from 0.3 to 0.8 μl l^{-1} SO_2, while the increase was 30% (1.9–2.5 s cm^{-1}) at 3.5 and 4 h. Thus $R_s^{SO_2}$ was responsive to SO_2 concentration independent of exposure time.

Residual Resistance to SO_2 Flux. At all SO_2 concentrations and exposure times, $R_r^{SO_2}$ was negative (Fig. 6). The range of $R_r^{SO_2}$ was −2.7 to −4.6 s cm^{-1}, with a mean of −3.2 s cm^{-1} ± 1.5 SD. With increasing exposure time, $R_r^{SO_2}$ became less negative, showing a 24 and 32% decline over time at 0.3 and 0.8 μl l^{-1} SO_2, respectively. The most negative $R_r^{SO_2}$ values were within the 1st h at the lowest and highest SO_2 concentrations (Fig. 6).

DISCUSSION

Estimates of $J^{SO_2}_{TOTAL}$ reported in the literature are influenced by plant species, SO_2 concentration in the atmosphere, and environmental conditions before and during exposure. The estimates of $J^{SO_2}_{TOTAL}$ in Table I, which are from representative herbaceous and shrub species exposed to SO_2 concentrations and environmental conditions similar to those used with *G. carolinianum*, range from 4 to 240 nmol cm^{-2} h^{-1}. For comparison, $J^{SO_2}_{TOTAL}$ in *G. carolinianum* extended from 27 to 67 nmol cm^{-2} h^{-1} of which 64 to 73% was the $J^{SO_2}_{INTERNAL}$ fraction. The remainder (27–36%) of $J^{SO_2}_{TOTAL}$ was attributed to leaf surface loss of SO_2. This latter percentage was comparable to that reported for other species using radioactively labeled SO_2 under laboratory conditions (12) and micrometeorological techniques in the field (37). With one exception (33), the data in Table I are from studies using mass balance techniques in gas exchange systems; the estimates of SO_2 flux using tissue sulfur levels (33) range from 5.3 to 42.2 nmol cm^{-2} h^{-1} in *P. vulgaris*. This range is likely to be an underestimate since the technique does not account for sulfur translocation out of the leaf or emission of H_2S.

The data for stomatal resistance to H_2O in *G. carolinianum* are important in using an analog model to estimate the role of a residual resistance in governing SO_2 flux into the leaf interior. Stomatal resistance to H_2O in *G. carolinianum* ranged from 2.9 to 4.0 s cm^{-1} and averaged 3.3 s cm^{-1}. These values compare favorably with the Körner *et al.* review (20) of minimum stomatal resistances to H_2O for vascular plant species in a number of morphological/ecological groupings. For shade-acclimated herbs from mesophytic habitats, the conditions under which *G. carolinianum* was grown, minimum values of stomatal resistance to H_2O for 90% of the literature studies ranged from 1.6 to 4.0 s cm^{-1} on a leaf area basis. For all plant groups, resistances were generally higher for plants grown under controlled *versus* natural environments. Thus, for *G. carolinianum* the measures of SO_2 flux and leaf resistance to H_2O are comparable to data reported for other herbaceous species under similar environmental and exposure conditions.

In the literature, the relationship between $J^{SO_2}_{INTERNAL}$ and $R_s^{SO_2}$ (as derived from H_2O) is not fully resolved. At least in part, $J^{SO_2}_{INTERNAL}$ is negatively correlated with $R_s^{SO_2}$ (15, 40). However, once the stomates open and the hydrated cell surfaces of the substomatal chamber and mesophyll tissue are exposed to the pollutant, the magnitude of $J^{SO_2}_{INTERNAL}$ may be dictated by the series of boundary layer, stomatal, and residual resistances. For *G. carolinianum*, the means of these individual components of leaf resistance to SO_2 flux were (in order) 0.3, 6.2, and −3.2 s cm^{-1}. Given resistances operating in series, SO_2 molecules experienced a net leaf resistance to diffusion into the leaf interior of +3.3 s cm^{-1}.

Black and Unsworth (2) present similar data for *Vicia faba*, although H_2S emissions were not factored into their calculations of SO_2 flux (flame photometry was measurement technique for total sulfur). Appropriately, they concluded that SO_2 did not experience a positive residual resistance (called an internal resistance); however, their data demonstrate a consistently negative $R_r^{SO_2}$. At $R_s^{SO_2}$ (*i.e.* 1.89 $R_s^{H_2O}$) values ≤ 5.0 s cm^{-1}, SO_2 experienced 10 to 18% less resistance than expected based upon analogy to H_2O. This percentage increased disproportionately so that, when $R_s^{SO_2} \geq 10$ s cm^{-1}, $R_s^{SO_2}$ was 30 to 40% less. Applying Eq. 5 from our methods, $R_r^{SO_2}$ in *V. faba* ranged from −0.3 to −5.0 s cm^{-1}. Using Black and Unsworth's technique (2), $R_r^{SO_2}$ in *G. carolinianum* would average −4.2 s cm^{-1}, 31% more negative than our mean $R_r^{SO_2}$ of −3.2 s cm^{-1}. As discussed below, the more negative $R_r^{SO_2}$ value calculated via the technique of Black and Unsworth (2) could be a consequence of not accounting for the emission of H_2S.

In a study of *Pinus sylvestris*, Hallgren *et al.* (15) reported a residual resistance to SO_2 flux that varied in magnitude and direction (positive and negative) but was generally positive during midday conditions. They observed light-dependent H_2S emissions and proposed that the additional sulfur (from H_2S) in the outlet air stream (and subsequent under estimation of SO_2 flux via mass-balance calculations) may account for the positive residual resistance. Using the midday data reported by Hällgren *et al.* (15), we calculate only a 20% reduction in $R_r^{SO_2}$ for *P. sylvestris* assuming maximum reported H_2S emissions. A comparable reparameterization of the analog model for SO_2 flux to *G. carolinianum* (equivalent to no discrimination of sulfur compounds in air stream), similarly makes $R_r^{SO_2}$ more negative by 19% (from −3.2

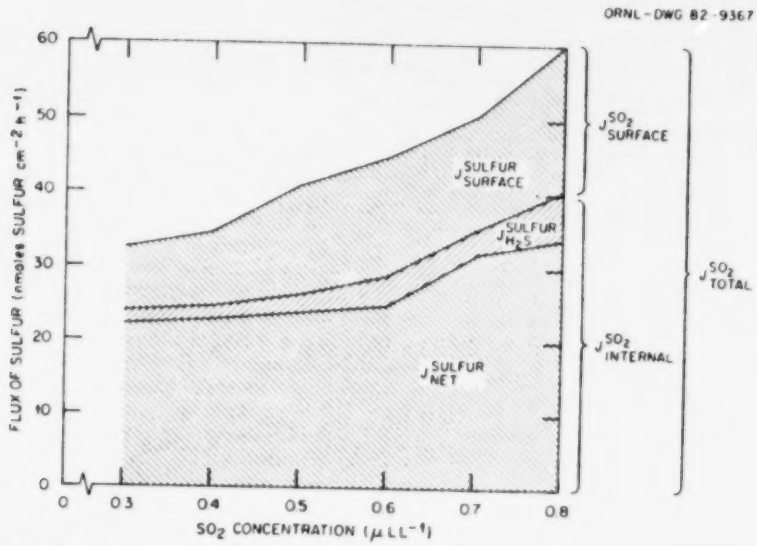

FIG. 4. Leaf budget of sulfur following exposure to SO_2 and the emission of H_2S. The data are expressed as nmol sulfur cm^{-2} h^{-1}, where nmol sulfur are equivalent to nmol of either H_2S or SO_2.

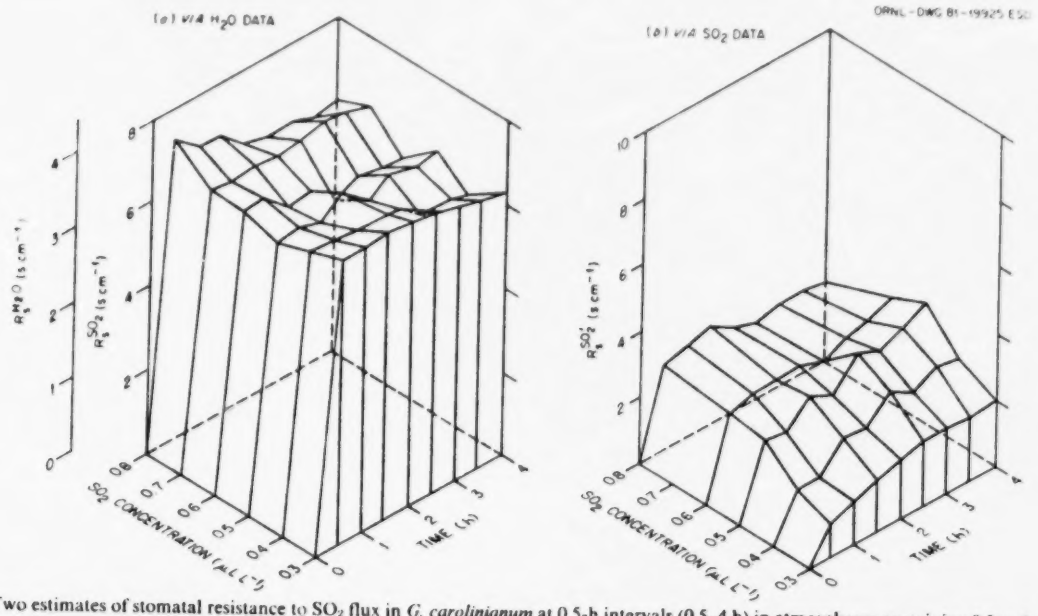

FIG. 5. Two estimates of stomatal resistance to SO_2 flux in *G. carolinianum* at 0.5-h intervals (0.5–4 h) in atmospheres containing 0.3 to 0.8 $\mu l\ l^{-1}$ SO_2. Stomatal resistance in 'a' ($R_s^{SO_2}$) is calculated via analogy to H_2O (Eq. 3), while the estimate in 'b' ($R_s^{SO_2}$) is calculated from the SO_2 data (Eq. 4).

to -3.8 s cm^{-1}).

In using Eq. 5 to estimate the role of $R_r^{SO_2}$, the SO_2 concentration in the leaf interior was set equal to zero ($C_i^{SO_2} = 0$), the coefficient of 1.89 provided the analogy between H_2O and SO_2 resistance in the boundary layer and stomate, and the leaf surface fraction of total SO_2 flux was determined during pollutant exposures in the dark. Black and Unsworth (2) concluded that $C_i^{SO_2}$ was zero in *V. faba*. The effect of a $C_i^{SO_2} > 0$ in *G. carolinianum* would be to make $R_r^{SO_2}$ more negative since the numerator in Eq. 4 (*i.e.* concentration gradient of SO_2) would be reduced. The analogy of SO_2 to H_2O as outlined in the Appendix is a common approach (2, 43, 46), although coefficient estimates range from 1.75 (18) to 2.03 (calculated from data in Ref. 10; rationale for estimation technique is provided in Refs. 9 and 34). The coefficient of 1.89 is an intermediate value and the use of either the lower or higher coefficient causes $R_r^{SO_2}$ to change only ±8%. Estimates of $J_{SURFACE}^{SO_2}$ at night were conducted on plants transpiring at rates 14 to 33% of maximum daylight values. The mean night:day ratio of $R_L^{H_2O}$ was 3.4, indicating substantial stomatal closure. If the stomates were not fully closed, a fraction of the $J_{SURFACE}^{SO_2}$ estimate would be flux into the leaf interior; as a consequence, values for $J_{SURFACE}^{SO_2}$ would be overestimates. The influence of an inflated $J_{SURFACE}^{SO_2}$ was evaluated using the analog model, by reducing the magnitude of leaf surface flux of SO_2 while leaving unchanged $J_{TOTAL}^{SO_2}$. Accordingly, $J_{INTERNAL}^{SO_2}$ was increased. A 30% reduction in $J_{SURFACE}^{SO_2}$ caused the mean $R_r^{SO_2}$ to become more negative (-3.2

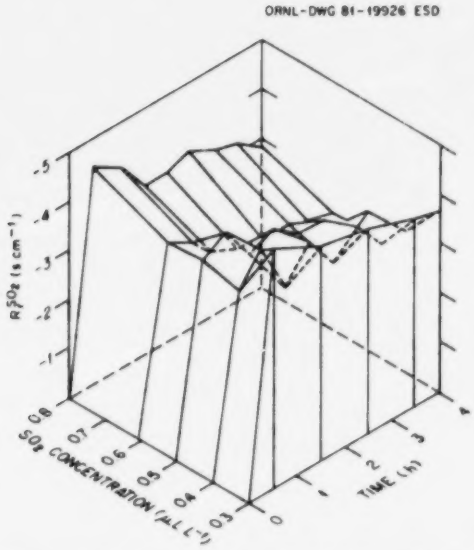

FIG. 6. Residual resistance to the flux of SO_2 into the leaf interior ($R_r^{SO_2}$).

Table I. *Examples of SO_2 Flux to Foliage of Herbaceous and Shrub Plant Species*

Fluxes are total leaf flux during light conditions.

Species	Technique[a]	SO_2 Flux[b]	Reference
		nmol cm^{-2} h^{-1}	
Medicago sativa	GE/MB	26.4–45.6	(35)
Diplacus aurantiacus	GE/MB	3.8–30.9	(46)
Heteromeles arbutifolia		7.5–41.3	
Petunia hybrida	GE/MB	4.0–7.0	(7)
Phaseolus vulgaris	TS	5.3–42.2	(33)
Phaseolus vulgaris	GE/MB	9.0–12.5	(25)
Helianthus annua	GE/MB	25–241.9	(29)

[a] Technique abbreviations are: GE/MB, gaseous exchange/mass balance; TS, tissue sulfur analysis.

[b] Where necessary, fluxes are recalculated on a leaf area basis and assume standard temperature and pressure.

to −3.4 s cm^{-1}) by only a 7% margin.

The emission of H_2S from foliage is a common response when sulfur additions are made to the atmosphere (5). Published H_2S emission rates exhibit a 10^4-fold range (Table II) and are greatest when exogenous sulfur compounds (*e.g.* SO_2, SO_4^{2-}) are administered near the metabolic site of sulfur reduction in the leaf (1). In *G. carolinianum*, a threshold SO_2 enrichment of 4.8 nmol cm^{-2} over 15 min appears necessary to induce detectable H_2S emissions from the leaf. Given a ratio of leaf internal to external area of 16 (28) and a uniform surface area per mesophyll cell of 4000 μm^2 (G. E. Taylor, Jr., unpublished observation), an SO_2 enrichment of 0.08 pmol per cell over 15 min is needed throughout the leaf interior to induce measurable amounts of H_2S. As with other observations (5, 36), this implies a prominent role for cell-mediated metabolic processes (*versus* gas phase diffusion) in governing H_2S emission kinetics. If H_2S in *G. carolinianum* was released from leaves as a plug at the start of SO_2 exposure with stomatal opening, H_2S concentration in the gas-exchange chamber would achieve a steady-state level theoretically within six air exchanges or 17 min given the chamber's mixing characteristics (40). The observed time to steady state (≥45 min) was nearly three times longer. This delay may reflect the time needed to activate enzymes of sulfur metabolism or the necessity of achieving a threshold level of SO_2 derivatives in mesophyll cells.

Table II. *Emission Rates of H_2S from Vegetation*

Examples are daylight emission rates.

Species	Sulfur Addition		H_2S Emission Rate[a]	Reference
	Organ	Sulfur Compound		
			nmol cm^{-2} h^{-1}	
Phaseolus vulgaris *Zea mays* *Lycopersicon esculentum*	Leaf	SO_2	0.8–1.4	(5)
Picea abies	Root	SO_4^{2-}	$1.0–10^{-2}$	(36)
Cucumis sp. *Curcurbita pepo* *Zea mays* *Glycine max* *Gossypium hirsutum*	Root and petiole	SO_4^{2-}	0.1–12.0	(45)
Glycine max	Root	SO_4^{2-}	[9.5–17] × 10^{-3}	(47)
Pinus sylvestris	Leaf	SO_2	0–0.8	(15)
Curcurbita pepo			0–4.4	(32)

[a] Where necessary, rates were recalculated on a leaf area basis and assuming standard temperature and pressure. Gravimetric emission rates (μg H_2S/g dry wt) were converted to a leaf area basis using a mg dry wt:cm^2 ratio of 2.24.

A residual resistance influencing the flux of SO_2 into the leaf interior is not surprising in light of comparable observations for a number of gases. Hill (16) demonstrated a direct relationship between pollutant uptake and the gas' solubility in water, thus inferring that flux was controlled in part by the rate of partitioning across the gas-to-liquid interface on the mesophyll cell surfaces. Other reports have demonstrated a positive residual resistance to leaf flux of mercury vapor (3), helium (8), and ozone (41).

The notable feature of $R_r^{SO_2}$ in *G. carolinianum* is its negative sign, which is also evident in the SO_2 data for *V. faba* (2) and inferred by the proposal of Klein *et al.* (19) regarding SO_2 flux in *P. sativum*. An analysis of the data comparing the fluxes to foliage of five different sulfur-containing gases (39) including SO_2 indicates that the negative character of the residual resistance is unique to SO_2 and not shared by other sulfur gases.

Because diffusive resistance is proportional to path length (27), the negative feature of $R_r^{SO_2}$ may be a consequence of an SO_2 mean diffusive path length in the gas phase that is less than that for H_2O. This proposal is comparable (but opposite in direction) to that for CO_2 in which the ratio of the mean path length for CO_2 relative to H_2O is greater than unity (17, 26). Whereas 70 to 80% of the H_2O molecules evaporate from cells of the substomatal cavity, only 10 to 20% of the CO_2 molecules are deposited within the same region (4). The longer path length for CO_2 in the gas phase reflects the molecule's lower solubility in water (30). For highly water-soluble gases such as SO_2, the ratio of diffusive path lengths for SO_2 *versus* H_2O may be less than unity. Given a leaf thickness in *G. carolinianum* of 150 μm (G. E. Taylor, Jr., unpublished results) and a H_2O path length of 60 μm (mean evaporation site two-thirds within the substomatal chamber), an SO_2 diffusion distance from the atmosphere to the leaf interior of 29 μm would account for the negative $R_r^{SO_2}$, given proportionality between resistance and diffusion distance. Thus, in contrast to influxing CO_2 (30, 31) and possibly other pollutant gases, the predominant site for SO_2 deposition in the leaf interior is the substomatal

chamber and not the mesophyll tissue. This preferential deposition of SO_2 may explain the intense selective localization of SO_2 products and cell injury in the stomatal complex (13, 44). This proposal also implies a significant role for internal leaf morphology/physiology in influencing both SO_2 flux to foliage (*e.g.* extent of cell surface area fronting substomatal chamber or water status of cell surfaces would affect magnitude of pollutant flux) and the equality of SO_2 deposition among spongy and palisades mesophyll tissue.

The flux of SO_2 across an air-water interface is noted by atmospheric chemists as being unique among the common pollutant gases (21). Resistance to diffusion of SO_2 in the gas phase is 20 to 30 times greater than that in the aqueous phase at physiological pH levels (21). This is markedly different from most gases, including CO_2, where exchange across the interface is controlled by resistance in the aqueous phase (22). The uniqueness of SO_2 transport is due to its high water solubility (40 times more soluble in water than CO_2) and subsequent chemical reactivity in solution (22). For SO_2 flux into the leaf interior, gas phase resistance (of which diffusive path length is a part) is the predominant factor governing pollutant uptake, while for CO_2 gas phase resistance is superimposed upon a significant aqueous phase resistance to transport. Given a prominent role for path length in contributing to SO_2 flux into the leaf interior, the 24 to 32% decline (less negative) in $R_r^{SO_2}$ with increasing exposure time in *G. carolinianum* (Fig. 5b) may be a consequence of an increasing SO_2 path length deeper into the substomatal chamber. This is consistent with the observation by Liss (21) that aqueous phase resistance to SO_2 flux becomes significant as the pH drops below 5, which may occur as the intense localized SO_2 deposition over time results in a progressive decline in the pH of the extracellular solution. A simultaneous comparison of leaf resistance to CO_2 and SO_2 may reveal the degree of covariance in respective leaf resistances among gases and thus the comparability of diffusive paths (25).

These results suggest a new appraisal of the role played by stomates in controlling SO_2 flux into the leaf interior. Changes in stomatal resistance to H_2O will affect, equally, transpiration and SO_2 flux only if the diffusive paths of SO_2 and H_2O are analogous: in *G. carolinianum*, the two pathways do not appear comparable in their entirety. Total leaf resistance to SO_2 flux into the leaf interior ($R_L^{SO_2}$) in *G. carolinianum* is as follows:

$$R_L^{SO_2} = 1.53\ R_s^{H_2O} + 1.89\ R_s^{H_2O} + (-R_r^{SO_2}) \qquad (6)$$

The residual resistance may arise from a mean SO_2 path in the gaseous phase that is shorter than that for H_2O.

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APPENDIX

Appendix - Analysis of sulfur dioxide flux *via* analogy to Ohm's Law.

Flux component	Abbreviation	Units	Technique	Comment
1. Total SO_2 flux to the leaf	$J^{SO_2}_{TOTAL}$	nmoles cm^{-2} h^{-1}	Experimentally measured	
2. SO_2 flux to the leaf surface	$J^{SO_2}_{SURFACE}$	nmoles cm^{-2} h^{-1}	Experimentally measured	
3. SO_2 flux to the leaf interior	$J^{SO_2}_{INTERNAL}$	nmoles cm^{-2} h^{-1}	$J^{SO_2}_{INTERNAL} = J^{SO_2}_{TOTAL} - J^{SO_2}_{SURFACE}$	
4. SO_2 concentration in the atmosphere	$C^{SO_2}_a$	nmoles cm^{-3}	Experimentally measured	
5. Boundary layer resistance to H_2O flux	$R^{H_2O}_a$	s cm^{-1}	Experimentally measured	
6. Stomatal resistance to H_2O flux	$R^{H_2O}_s$	s cm^{-1}	Experimentally measured	
7. Leaf resistance to H_2O flux	$R^{H_2O}_L$	s cm^{-1}	$R^{H_2O}_L = R^{H_2O}_a + R^{H_2O}_s$	
8. Boundary layer resistance to SO_2 flux	$R^{SO_2}_a$	s cm^{-1}	$R^{SO_2}_a = 1.63\ R^{H_2O}_a$	Assumes resistance is a function of ratio of the diffusion coefficients of the two gases in air to the 2/3 power (41).
9. Stomatal resistance to SO_2 flux	$R^{SO_2}_s$	s cm^{-1}	$R^{SO_2}_s = 1.89\ R^{H_2O}_s$	Assumes resistance is a function of ratio of the diffusion coefficients of the two gases in air (41).
10. Leaf surface resistance to SO_2 flux	$R^{SO_2}_e$	s cm^{-1}	$R^{SO_2}_e = C^{SO_2}_a (J^{SO_2}_{SURFACE} - R^{SO_2}_a)^{-1}$	Assumes liquid-phase SO_2 concentration on leaf surface ($C^{SO_2}_e$) is zero.
11. SO_2 concentration at leaf surface (gas-phase)	$C^{SO_2}_c$	nmoles cm^{-3}	$C^{SO_2}_c = C^{SO_2}_a - (J^{SO_2}_{SURFACE} * R^{SO_2}_a)$	
12. SO_2 concentration in intercellular space	$C^{SO_2}_{ic}$	nmoles cm^{-2} h^{-1}	$C^{SO_2}_{ic} = C^{SO_2}_c - R^{SO_2}_s * J^{SO_2}_{INTERNAL}$	
13. Stomatal resistance to SO_2 flux (model calculation)	$R^{SO_2}_s{}'$	s cm^{-1}	$R^{SO_2}_s{}' = C^{SO_2}_c (J^{SO_2}_{INTERNAL})^{-1}$	Assumes liquid-phase SO_2 concentration in leaf interior ($C^{SO_2}_i$) is zero.
14. Residual resistance to SO_2 flux	$R^{SO_2}_r$	s cm^{-1}	$R^{SO_2}_r = R^{SO_2}_s{}' - R^{SO_2}_s$	This calculation is the difference between two methods of calculating stomatal resistance to SO_2 flux (#9 and 13).
15. Leaf resistance to SO_2 flux	$R^{SO_2}_L$	s cm^{-1}	$R^{SO_2}_L = 1.63\ R^{H_2O}_a + 1.89\ R^{H_2O}_s + R^{SO_2}_r$	
16. H_2S concentration in the atmosphere	$C^{H_2S}_a$	nmoles cm^{-3}	Experimentally measured	
17. Efflux rate of H_2S	J^{H_2S}	nmoles cm^{-2} h^{-1}	Experimentally measured	
18. Stomatal resistance to H_2S flux	$R^{H_2S}_s$	s cm^{-1}	$R^{H_2S}_s = 1.37\ R^{H_2O}_s$	See # 9.
19. Boundary layer resistance to H_2S flux	$R^{H_2S}_a$	s cm^{-1}	$R^{H_2S}_a = 1.24\ R^{H_2O}_a$	See # 8.
20. H_2S concentration in the intercellular space	$C^{H_2S}_{ic}$	nmoles cm^{-3}	$C^{H_2S}_{ic} = C^{H_2S}_a + J^{H_2S} * (R^{H_2S}_s + R^{H_2S}_a)$	
21. Net flux of sulfur to leaf interior (liquid-phase)	J^{Sulfur}_{NET}	nmoles S cm^{-2} h^{-1}	$J^{Sulfur}_{NET} = J^{SO_2}_{INTERNAL} - J^{H_2S}$	